

is on the opposite side to the side where the rays such as solar rays enter.

[CLAIM 13] The solar battery unit as set forth in claim 11, characterized in that the space between the first substrate and the second substrate is filled with an inert gas such as argon gas.

[CLAIM 14] The solar battery unit as set forth in claim 11, characterized in that at least one of the first substrate and the second substrate on the side where rays such as solar rays enter is a transparent substrate or a translucent substrate formed of glass, plastic or resin.

[CLAIM 15] The solar battery unit as set forth in claim 11, characterized in that an anti-reflection film is coated or arranged on the top surface or bottom surface of at least one of the first substrate and the second substrate on the side where rays such as solar rays enter.

[CLAIM 16] The solar battery unit as set forth in claim 11, characterized in that a light catalyst film made of titanium dioxide (TiO_2) or the like is coated or arranged on the top surface of at least one of the first substrate and the second substrate on the side where rays such as solar rays enter.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[TECHNICAL FIELD OF THE INVENTION]

The present invention relates to a semiconductor, a solar battery employing it, and a manufacturing method thereof.

[0002]

【PRIOR ART】

Conventionally, as a power source which is harmless to the environment, attention has been being paid to solar batteries employing silicon. As for the solar batteries employing silicon, while there is known a monocrystalline silicon type solar battery which is used in artificial satellites or the like, as practical ones a solar battery employing polycrystalline silicon and a solar battery employing amorphous silicon have already been practically used in industry and at home.

【0003】

However, since these solar batteries employing silicon use a vacuum process such as CVD (chemical vapor deposition) process or the like, manufacturing cost is high, and since a great deal of quantity of heat and a great deal of electricity are used in the process, the balance between the energy required for manufacturing and the energy generated by the solar battery is very poor, and thus it has not been necessarily true that they are energy-saving power sources.

【0004】

On the other hand, a new type solar battery which is referred to as the so-called "wet solar cell" or "fourth-generation photocell" was proposed in 1991 by Gletzel et al. In this wet solar cell, as shown in Fig. 7, titania (titanium dioxide) 701 which is a semiconductor is used as one electrode, and platinum electrode, ITO or the like is used as the other electrode 702, and iodine or the like is used for an electrolyte solution 703 between these electrodes. As for a reaction principle, the titania (TiO_2) that is a semiconductor, which has received rays such as solar rays

receives electrons to deliver them to the electrodes, and holes (h^+) which are left in the titania electrode then reduce iodine ions to convert I^- into I_3^- . The iodine ions which have been reduced receive the electrons again to be oxidized at the counter electrode, and thus they are cyclically moved between both the electrodes, thereby realizing the battery.

[0005]

In this wet solar cell, when only titania is used as an electrode, only ultraviolet rays in solar rays can be effectively utilized. Therefore, the titania is mixed with organic dye or the like to sensitize so as to absorb rays up to the visible ray region. For this reason, such one is generally called as a dye-sensitized solar cell. Such a wet solar cell is greatly expected to be a low cost solar battery, since its material is inexpensive and it does not need a large scale equipment such as one for the vacuum process and the like.

[0006]

[PROBLEM TO BE SOLVED BY THE INVENTION]

However, although this dye-sensitized solar cell contains organic dye in the titania electrode for sensitizing to the absorption wavelength of solar rays, the dye is decomposed by titania over time because titania is so-called photocatalyst. Therefore, the dye-sensitized solar cell can not have a practical life as a solar battery. Further, when a flat plate-shaped titania electrode is simply used, practical current and voltage can not be secured because of its small absorption area of solar rays.

[0007]

[MEANS FOR SOLVING THE PROBLEM]

A solar battery employing a titanium dioxide semiconductor of the present invention is characterized in that the surface of the titanium dioxide semiconductor and inside of the titanium dioxide semiconductor are formed with pores, and the titanium dioxide semiconductor is held between one pair of electrodes, and the titanium dioxide semiconductor and at least one of the pair of electrodes form a rectification barrier.

[0008]

Said rectification barrier is characterized in that it is the Schottky barrier being formed by contacting the titanium dioxide semiconductor with the metallic electrode which is at least one of said pair of electrodes.

[0009]

The metallic electrode with which said titanium dioxide semiconductor forms the Schottky barrier is characterized by being formed in such a way as to penetrate into the pores formed in the surface of the titanium dioxide semiconductor and inside of the titanium dioxide semiconductor.

[0010]

Said titanium dioxide semiconductor is characterized in that it is an anatase type titanium dioxide which has a porosity of 5 to 90%.

[0011]

The metallic electrode with which said titanium dioxide semiconductor forms the Schottky barrier is characterized by being a transparent electrode made of ITO or the like, or a metal such as Al, Ni, Cr, Pt, Ag, Au, Cu, Mo, Ti, and Ta, or a metallic alloy made of one or more of them.

[0012]

Said electrodes are characterized by being formed by vacuum evaporation method.

[0013]

Said electrodes are characterized by being formed by sputtering method.

[0014]

Said electrodes are characterized by being formed by printing method.

[0015]

Said titanium dioxide semiconductor is characterized by including impurities such as Cr and/or V.

[0016]

Said titanium dioxide semiconductor is characterized by including Mo.

[0017]

A solar battery unit of the present invention which employs a titanium dioxide (TiO_2) semiconductor is characterized in that the solar battery unit comprises a solar battery which is comprised of a titanium dioxide semiconductor being held between one pair of electrodes and being formed with pores in the surface of the titanium dioxide semiconductor and inside of the titanium dioxide semiconductor; and a first substrate and a second substrate which hold the solar battery.

[0018]

The solar battery unit is characterized in that a reflection film is coated or arranged for reflecting rays such as solar rays on at least one of the first substrate and the second substrate which is on the opposite side to the side where the rays such as solar rays enter

[0019]

The solar battery unit is characterized in that the space between the first substrate and the second substrate is filled with an inert gas such as argon gas.

[0020]

The solar battery unit is characterized in that at least one of the first substrate and the second substrate on the side where rays such as solar rays enter is a transparent substrate or a translucent substrate formed of glass, plastic or resin.

[0021]

The solar batter unit is characterized in that an anti-reflection film is coated or arranged on the top surface or bottom surface of at least one of the first substrate and the second substrate on the side where rays such as solar rays enter.

[0022]

The solar battery unit is characterized in that a light catalyst film made of titanium dioxide (TiO_2) or the like is coated or arranged on the top surface of at least one of the first substrate and the second substrate on the side where rays such as solar rays enter.

[0023]

[EMBODIMENT OF THE INVENTION]

Next, embodiments according to the present invention will be described in detail with reference to the accompanying drawings. Fig. 1 to Fig. 6 are drawings which schematically show the structures, the circuit and the like of a solar battery according to the present invention.

[0024]

(First Embodiment)

Fig. 1 is a schematic diagram which schematically shows the structure of a solar battery cell 100 which is an embodiment of a solar battery employing a semiconductor according to the present invention.

[0025]

A first electrode 103 is formed from a transparent electrode made of ITO or the like, or a metallic electrode (which is made of a metal such as Al, Ni, Cr, Pt, Ag, Au, Cu, Mo, Ti and Ta, or an alloy made of one or more of them).

[0026]

An anatase type titanium dioxide (TiO_2) semiconductor 101 is formed on the first electrode 103.

[0027]

A comb-shaped (stripe-like) second electrode 102 is formed on the anatase type titanium dioxide (TiO_2) semiconductor 101. Although only three electrode teeth are illustrated in Fig.1, actually, there are a more number of stripe-like comb-shaped electrode teeth.

[0028]

The second electrode 102 is formed from a transparent electrode made of ITO or the like, or a metallic electrode (which is made of a metal such as Al, Ni, Cr, Pt, Ag, Au, Cu, Mo, Ti, and Ta, or an alloy made of one or more of them).

[0029]

Since the titania semiconductor 101 is in contact with the above-mentioned first electrode or the above-mentioned second electrode, the Schottky barrier which has a height corresponding to the difference in the work function between the titania semiconductor 101 and the above-mentioned first

electrode or the above-mentioned second electrode is formed in the interface therebetween, so that rectification function occurs.

[0030]

For example, when the titanium dioxide (TiO_2) semiconductor is in contact with the second electrode 102 and the work function of the second electrode 102 is larger than that of the titanium dioxide (TiO_2) semiconductor, rectification function occurs.

[0031]

The situation can be represented with an equivalent circuit, and as shown in Fig. 2, a circulation circuit of a current including a diode 210 is formed.

[0032]

In this case, when rays such as solar rays strike the titania semiconductor 101, electrons are excited in the titania semiconductor to generate electrons and holes (positive holes). The generated electrons and holes (positive holes) generate a current, thereby forming a loop of the current in the solar battery as shown in the equivalent circuit of Fig. 2.

[0033]

Fig. 3 and Fig. 4 show the structure of the solar battery of the embodiment according to the present invention.

[0034]

Fig. 3 shows the situation in which solar rays strike a part of the titanium dioxide (TiO_2) semiconductor where no metallic electrode 102 of the solar battery shown in Fig. 1 is formed.

[0035]

Fig. 4 shows the situation in which solar rays strike the metallic electrode 102 of the solar battery shown in Fig. 1 and a part of the titanium dioxide (TiO_2) semiconductor where no metallic electrode 102 is formed.

[0036]

In Figs. 3 and 4, each of the arrows indicates the traveling direction of the ray, and the situation in which the rays enter the surface and pores of the titanium dioxide semiconductor is shown.

[0037]

As shown in Fig. 4, the titanium dioxide (TiO_2) semiconductor is in contact with the metallic electrode 402 to form the Schottky barrier.

[0038]

In this case, the metallic electrode 402 formed on the surface of the titanium dioxide (TiO_2) semiconductor is formed to penetrate into the pores of the titanium dioxide (TiO_2) semiconductor 401, as shown in Fig. 4. By doing so, the surface area of the Schottky barrier which is formed between the metal (the metallic electrode 402) and the semiconductor (the titanium dioxide (TiO_2) semiconductor 401) is increased.

[0039]

The metallic electrode 402 which is formed on the surface of the titanium dioxide (TiO_2) semiconductor is formed from a transparent electrode made of ITO or the like, or a metal such as Al, Ni, Cr, Pt, Ag, Au, Cu, Mo, Ti and Ta, or an alloy made of one or more of them, and is formed on the surface of the titanium dioxide (TiO_2) semiconductor by the vacuum evaporation method, the sputtering method or the printing method or the like.

[0040]

As described above, since the titanium dioxide (TiO_2) semiconductor of the present invention has a very large porosity, solar rays enter not only the surface of the titanium dioxide (TiO_2) semiconductor but also the pores of the titanium dioxide (TiO_2) semiconductor, and they cause multiple-reflection repeatedly within the pores as indicated by the arrows in Fig. 3 and Fig. 4 to cause the photovoltaic effect in the titanium dioxide (TiO_2) semiconductor.

[0041]

Specifically, since interface potential is present in the contact part between the metal and the semiconductor (the Schottky barrier part), which provides the rectification function, to produce electric field for the barrier, when rays (photons) having larger energy than the gap between the valence band and the conduction band enter the vicinity of the interface, the electrons and the positive holes which have been generated are drawn apart due to the electric field of the interface, thereby causing potential difference (photoelectromotive force).

[0042]

Therefore, if an external circuit as shown in Fig. 2 is connected to the contact part (the Schottky barrier part), a photo-exciting current is obtained, thereby providing a solar battery.

[0043]

Note that, as shown in Fig. 3 and Fig. 4, the rays which have entered the pores of the titanium dioxide semiconductor are reflected repeatedly in the pores, and a part of the rays pass through downwardly but they are reflected by the flat

surface lower electrode 103 shown in Fig. 1, or by a reflecting plate 614 shown in Fig. 6, and reenter the surface or the pores of the titanium dioxide semiconductor, thereby causing the photoelectromotive force.

[0044]

Although a detailed description with regard to the manufacturing method of the titania semiconductors 301, 401 will be made later, the titania semiconductors 301 and 401 are the oxide semiconductors made of an anatase type titanium dioxide which is formed by sintering fine powder of titanium (Ti) having the particle size of about 20 nm to 100 μ m for oxidizing it, or the oxide semiconductors which are formed by sintering fine powder of an anatase type titania (TiO_2) having the particle size of about 20 to 2,000 nm.

[0045]

The titanium dioxide semiconductor 301 or 401 has a very high porosity (void ratio), and more specifically, it is formed from an anatase type titania semiconductor having a porosity (void ratio) of 5 to 90 %. The titanium dioxide semiconductor 301 or 401 is an anatase type titania semiconductor which preferably has a porosity (void ratio) of 15 to 50 %, and more preferably, has a porosity of 20 to 40 %.

[0046]

Such an extremely high porosity (void ratio) remarkably increases the surface area of the titania as compared with the case where the titania electrode is formed into a flat-shaped plate. For example, the total surface area of titanium dioxide in an area of 1 cm^2 can be made 1,000 to 10,000 cm^2 . As a result, since the contact area between the

titania and solar rays is also increased, 1,000 to 10,000 times current will mathematically occur.

[0047]

Fig. 5 shows the structure of the titania semiconductor of the embodiment according to the present invention.

[0048]

The titania semiconductor 501 contains 0.1 to 2.5 $\mu\text{mol/g}$ of a very small quantity of impurities such as Cr (chromium) and V (vanadium) for sensitizing to the absorption wavelength of rays such as solar rays, and more ideally, it is preferable that it contains 1.5 to 2.0 $\mu\text{mol/g}$ of impurities such as Cr and V.

[0049]

In this way, since it contains a very small quantity of Cr or V as impurities, it is possible to absorb the visible rays of 400 nm or longer (normally, this means the rays having the wavelength of 400 to 750 nm) which can not be efficiently absorbed by the normal titania semiconductor, thereby greatly increasing the efficiency of the solar battery.

[0050]

Further, in contrast to a conventional dye-sensitized solar cell, since organic dye is not used for sensitizing to the absorption wavelength of solar rays, there is not the drawback about the life of solar battery in that the organic dye is decomposed by titania which is photocatalyst, thereby enabling the life of solar battery to be significantly increased.

[0051]

The titania electrode 501 contains impurities such as Cr and V for sensitizing to the absorption wavelength of rays

such as solar rays, and in this case by sintering a titania (titanium dioxide) electrode so as to have a condition in which Ti in titanium dioxide substitutes for Cr or V as shown in Fig. 5, it becomes possible to absorb the visible rays of 400 nm or longer which can not be absorbed by the normal titania electrode, to thereby be able to absorb solar rays at a practical level.

[0052]

(Second Embodiment)

The titania semiconductor which is employed in the present invention is formed by the so-called Powder Injection Molding method (in general, it is called the PIM method), or the so-called Metal Injection Molding method (in general, it is called the MIM method).

[0053]

Specifically, a resin binder of 99 to 50 % in the volume ratio is added to titanium fine powder having the particle size of about 20 to 2,000 nm, and then they are kneaded to form a source compound having the low viscosity (1,000 to 3,000 P) with which enables the injection molding.

[0054]

At this time, Cr or V to be added to the source compound in order to increase the absorption wavelength width of rays may be added thereto either in the state of the oxide of Cr (CrO_3) or the oxide of V, or in the state of pure Cr or pure V.

[0055]

Thereafter, following the debinding process for removing the resin binder (degreasing process), the debound titanium fine powder is sintered together with the

above-mentioned additive. The titanium fine powder is oxidized through this sintering process to become the anatase type titania (titanium dioxide).

[0056]

In this case, since titania is thermally stable in rutile and the crystal structure of the anatase is changed into rutile through heating at the temperature of equal to or higher than 900 degrees, the temperature during the above-described debinding process and the above-described sintering process must be equal to or lower than 900 degrees, and sintering and oxidation must be carried out under such condition such that titanium can keep the crystal structure as the anatase type oxide.

[0057]

In addition, in the sintering process, in order to make an alloy of titania without the anatase type crystal structure being destroyed, MoO_3 (molybdenum oxide) having the melting point of 795 degrees is added in advance as a sintering assistant to the source compound to make the sintered alloy of titania. This sintering assistant is not limited to MoO_3 (molybdenum oxide), and any one can be utilized as long as its melting point is equal to or lower than 900 degrees.

[0058]

Alternatively, as for a method of obtaining the anatase type titanium dioxide semiconductor without any sintering assistant being employed, titanium dioxide semiconductor may be also formed by sintering titanium fine powder in a vacuum atmosphere at the temperature of about 1,200 degrees once, and then resintering the titanium in an oxygen atmosphere at the temperature of equal to or lower than 900 degrees to

oxidize.

[0059]

(Third Embodiment)

Fig. 6 shows an actual example of a module (unit) of the solar battery of the present invention.

[0060]

A semiconductor 601 made of titanium dioxide is held between one pair of electrodes consisting of an upper electrode 602 and a lower electrode 603. These electrodes are formed from a transparent electrode made of ITO or the like, or a metallic electrode (which is made of a metal such as Al, Ni, Cr, Pt, Ag, Au, Cu, Mo, Ti and Ta, or an alloy made of one or more of them).

[0061]

The upper electrode 602 is a stripe-like comb-shaped electrode consisting of a plurality of electrode teeth, and rays such as solar rays strike a part of the titanium dioxide semiconductor where the upper electrode is not formed.

[0062]

The lower electrode 603 may be either a flat surface electrode which is in contact with the titanium dioxide semiconductor, as shown in Fig. 1, or a stripe-like comb-shaped electrode or the like which is not a flat surface electrode, as shown in Fig. 6.

[0063]

The solar battery comprised of the titanium dioxide semiconductor which is held between the pair of electrodes is accommodated in the space between an upper substrate 612 and a lower substrate 615 which are made of transparent glass, plastics, resin or the like, and is sealed with a sealing

material 613. An inert gas such as argon (Ag) may be filled between the two substrates.

[0064]

A reflecting film may be formed on the lower substrate 615 so as to reflect rays which have passed through the titanium dioxide semiconductor towards the titanium dioxide semiconductor again.

[0065]

Further, in order to increase the amount of light entering the solar battery comprised of the titanium dioxide semiconductor, an antireflection film 612 is applied to the top surface or the bottom surface of the upper substrate.

[0066]

Furthermore, the uppermost surface of the upper substrate is coated with a thin film of titanium dioxide (TiO_2) having photocatalyst function. Since the solar battery of the present invention is often placed out-doors for electric power generation, by coating the upper substrate (cover glass) of the solar battery of the present invention with the thin film of titanium dioxide (TiO_2), the cover glass of the solar battery can be prevented from becoming dirty and being contaminated due to carbon dioxide exhausted from automobiles and the like and organic contaminants.

[0067]

As described above, according to the present invention, in a solar battery employing a titanium dioxide (TiO_2) electrode, since the titanium dioxide electrode has a porosity of 5 to 90 %, the porosity can be made extremely high, and the surface area of the titania is remarkably increased as compared with the conventional wet solar battery in which

a titania electrode is formed into a flat-shaped plate. Specifically, the total surface area of titania fine powder in an area of 1 cm² can be made 1,000 to 10,000 cm². This increases also the contact area between the titania fine powder and solar rays, so that 1,000 to 10,000 times current will mathematically occur.

[0068]

Further, since the above-described titanium dioxide semiconductor contains 0.1 to 2.0 μmol/g of impurities such as Cr or V, it is possible to absorb the visible rays of 400 nm or longer (normally, this means the rays having the wavelength of 400 to 750 nm) which can not be efficiently absorbed by the normal titania electrode, so that the efficiency of the solar battery can be greatly improved.

[0069]

Furthermore, in contrast to the conventional dye-sensitized solar cell, since organic dye is not used for sensitizing to the absorption wavelength of solar rays, there is not a drawback about the life of solar battery in that organic dye is decomposed by titania which is photocatalyst, thereby enabling the life of solar battery to be significantly increased.

[BRIEF DESCRIPTION OF THE DRAWING]

[Fig.1] Fig.1 is a schematic diagram which schematically shows the structure of a solar battery of an embodiment according to the present invention.

[FIG.2] Fig.2 is a diagram which shows an equivalent circuit of the solar battery of the embodiment according to the present invention.

[FIG.3] Fig.3 is a schematic sectional view which schematically shows the structure of the solar battery of the embodiment according to the present invention.

[FIG.4] Fig.4 is a schematic sectional view which schematically shows the structure of the solar battery of the embodiment according to the present invention.

[Fig.5] Fig.5 is a schematic sectional view which schematically shows the structure of the solar battery of the embodiment according to the present invention.

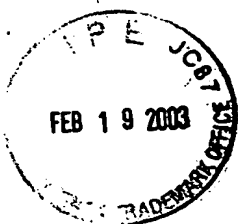
[Fig.6] Fig.6 is a schematic sectional view which schematically shows the structure of a solar battery module (unit) of an embodiment according to the present invention.

[Fig.7] Fig.7 is a schematic diagram which schematically shows the structure of a conventional solar battery.

[EXPLANATION OF THE REFERENCE NUMERALS]

101, 301, 401, 501, 601	titania semiconductor
102, 402, 502, 602	second electrode
103, 503, 603	first electrode
104, 504	substrate

【Name of the Document】	Application for Patent	
【Our Reference】	J0077366	
【Filing Date】	December 27, 1999	
【Attention】	The Director General of JPO	
【International Classification】	B01J 35/04	
	B01J 37/00	
【Inventor】		
【Address】	c/o Seiko Epson Corporation	
	3-5, Owa 3-chome, Suwa-shi, Nagano-ken, Japan	
【Name】	Yuji FUJIMORI	
【Applicant】		
【Identification No.】	000002369	
【Name】	Seiko Epson Corporation	
【Representative】	Hideaki YASUKAWA	
【Attorney】		
【Identification No.】	100093388	
【Patent Attorney】		
【Name】	Kisaburo SUZUKI	
【Telephone No.】	0266-52-3139	
【Attorney to be designated】		
【Identification No.】	100095728	
【Patent Attorney】		
【Name】	Masataka KAMIYANAGI	
【Attorney to be designated】		
【Identification No.】	100107261	
【Patent Attorney】		
【Name】	Osamu SUZAWA	
【Identification of Payment】		
【Prepayment Registration Number】	013044	
【Amount of Payment】	JP¥ 21,000	
【List of the Submitted Documents】		
【Name of Document】	Specification and Claims	1
【Name of Document】	Drawings	1
【Name of Document】	Abstract	1
【Number of General Power of Attorney】	9711684	
【Proof is required or not】	Proof is required	



VERIFICATION

I, Kazuo Asahi, of Asahi & Masuda of Nishi-Shinbashi Noa Building 4F & 5F of 18-9, Nishi-Shinbashi 1-chome, Minato-ku, Tokyo 105-0003 Japan do solemnly and sincerely verify that I understand well both Japanese and English languages and that the attached document in English language is full and faithful translation of the copy of Japanese Patent Application No. 11-371207 filed on December 27, 1999.

Kazuo Asahi

Date: February 4, 2003

RECEIVED
FEB 24 2003
TC 2800 MAIL ROOM